Chapter 1 INTRODUCTION AND SUMMARY

1.1 Low-dimensional materials, TCNQ salts

In the past three decades, the physics and chemistry of low-dimensional materials have attracted considerable attention[1/2]. The interest stems from the possibility to study specific low-dimensional effects connected with the characteristic electronic structure of these systems. Furthermore, their theoretical treatment is less complex than for three-dimensional systems. To date, a major accomplishment of the joint endeavour of physicists and chemists is the discovery of a number of "molecular" superconductors[3]. Although superconductivity has not been found at high temperatures as originally anticipated[4], the huge number of experimental and theoretical investigations in the field have contributed greatly to a comprehension of the "low-dimensional" solid state.

An extensively studied class of low-dimensional materials comprises the pseudo one-dimensional crystals of the charge transfer salts of the organic electron acceptor 7,7,8,8-tetracyano-p-quinodimethane (TCNQ,I). TCNQ forms

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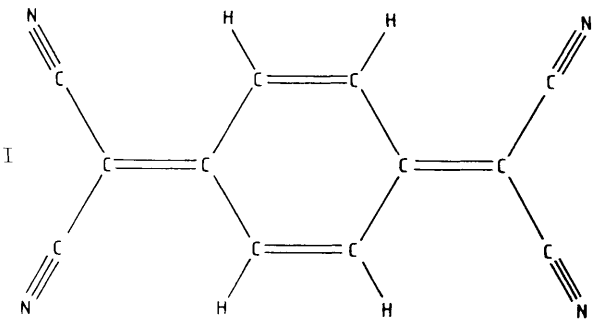


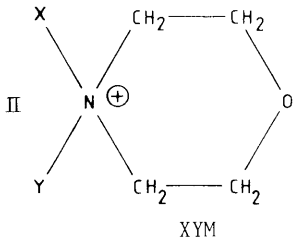
TCNQ

crystalline complexes with a large variety of both organic and inorganic donors[5]. The stoichiometry of donor to TCNQ is 1:1 in simple salts, whereas complexes with other compositions (i.e. 1:2, 2:3, etc.) are called complex salts. The crystals contain either isolated (groups of) TCNQ molecules, or linear arrays in which the planar TCNQ molecules are piled face-to-face in segregated stacks. Only the latter group may show one-dimensional behaviour and will be considered in the present thesis. The compounds will be referred to in short as TCNQ complexes or TCNQ salts.

The TCNQ salts exhibit a large variation in electronic properties[1/2] and in crystal packing[6/7]. Based on the observed electrical conductivities, Torrance[8] has given an empirical classification, which distinguishes simple and complex salts, with either complete or incomplete transfer of charge from donor to TCNQ. In this approach, the physical behaviour predominantly depends on whether ρ, the (average) number of unpaired electrons per TCNQ molecule, is 1 (class I), a simple rational fraction (class III), or irrational (classes II and IV). Although this gives a main classification of TCNQ salts, large differences within the classes are still found, which must be accounted for by other important parameters. For example, the room temperature electrical conductivities of the class III salts span a range of 6 orders of magnitude. Moreover, phase transitions are encountered, which leave ρ unchanged, but are accompanied by drastic changes in physical properties.

1.2 Scope of this thesis

The present thesis is part of a project in which the relations between crystal structures and physical properties of TCNQ salts containing chemically closely related donor molecules are studied in a systematic way. As cations N-X,N-Y-(thio)morpholinium (XY(T)M,II) groups are taken, where X and Y stand for



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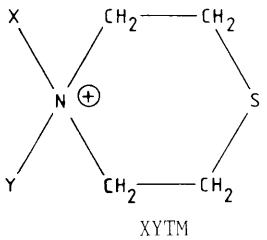


XYTM

hydrogen or simple alkyl groups. The TCNQ complexes of these cations will be referred to as XY(T)M salts. The charge transfer from the donors is assumed to be complete. Emphasis will be put on the complexes with a stoichiometry of 1:2 with, consequently, $\rho = \frac{1}{2}$.

By taking closely related donors, the number of factors influencing the differences in physical properties, is limited as much as possible. In the XY(T)M salts considered, differences are only due to replacement of O by S, and to the increasing length of the homologous X and Y substituents. Nevertheless, these minor changes turn out to be significant enough to bring about a large diversity of crystal structures and physical properties.

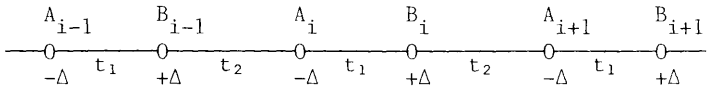
The work on measurements and interpretation of the physical properties of the XY(T)M salts is mainly concentrated in the Department of Physical Chemistry of the University of Groningen. The results used here were, or will be, published more extensively elsewhere[9/10]. A crystallographic basis for the work has been provided in the crystal chemistry group of the Department of Chemical Physics. Van Bodegom[7] has given a classification, based essentially on size and shape of the cations, of all the crystal structures of TCNQ salts with segregated stacks, determined up to 1979. The present thesis is a continuation of the study of the crystal structures of $XY(T)M(TCNQ)_2$ salts, and aims at establishing their impact on the physical behaviour. This aim has been approached as follows:

- determination of the crystal structure of a large number of complexes, selected on the basis of their physical behaviour, from a group of newly synthesized salts.
- classification of the structures according to their electrical and magnetic properties, in combination with a qualitative discussion of the observed regularities in terms of the structural details. A brief summary of the necessary theoretical concepts and definitions will be given in the following section. A more quantitative physical approach will be given by Oostra[10].
- study of phase transitions by structure determinations above and below the transition points, and by X-ray diffuse scattering experiments near these points. The latter study has been limited mainly to the development of equipment necessary for this type of work.

1.3 Theoretical concepts and physical behaviour

1.3.1 Band model

In the TCNQ salts with segregated stacks, the π-systems of successive molecules in a stack overlap, which gives rise to a pseudo one-dimensional electron band containing the charge transferred from the donors. As a model for the stacks in the $XY(T)M(TCNQ)_2$ salts, we consider a linear chain in which molecules A and B alternate. The average number of electrons per molecule, ρ, is $\frac{1}{2}$. Since each molecular site can be occupied by two electrons with opposite spin, the chain is called a quarter filled band system. Successive entities -A-B are translationally equivalent. A periodic potential field, with values of $-\Delta$ at A and $+\Delta$ at B, causes an uneven distribution of the electrons. Transfer integrals between neighbouring sites are t_1 and t_2, and we choose $t_1 > t_2$.



Construction of a tight-binding band of non-interacting electrons, gives the energy spectrum of Fig.1.1[10]. Since $\rho = \frac{1}{2}$, the lower band is half-filled and for all values of t_1, t_2 and Δ the system is metallic, i.e. the electrons in the highest filled energy levels can be readily promoted to unoccupied levels that are only infinitesimally higher in energy. The charges ρ_A and ρ_B at the molecular sites are given by the square of the relevant coefficients in the wave function of the system. The charge alternation $\Delta\rho = \frac{1}{2}(\rho_A - \rho_B) = \rho_A - \frac{1}{2}$ is given[11] by

$$\Delta\rho = \frac{p}{2\pi} \frac{\Delta}{\sqrt{(t_1 + t_2)^2 + \Delta^2}} \int_0^{\frac{\pi}{2}} \frac{d\Theta}{\sqrt{1 - m \sin^2\Theta}} \qquad (1.1)$$

where

$$m = \frac{4t_1t_2}{\Delta^2 + (t_1 + t_2)^2} \leq 1 \quad \text{and} \quad p = 4$$

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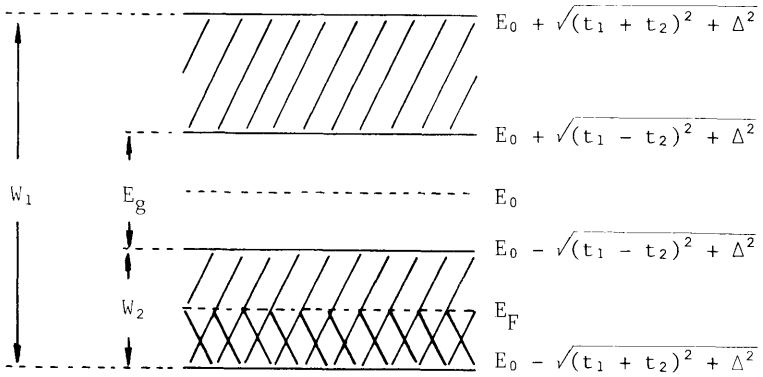

Fig.1.1 Energy levels of the linear chain.
E_g is the band gap
W_1 and W_2 are the band widths.

Both electrical and magnetic behaviour of the $XY(T)M(TCNQ)_2$ salts indicate[9] that electron correlations, which are ignored in the above model, confound the validity of one-electron theory for these salts. These correlations stem from the Coulomb interactions between electrons in the band, and are described by U_0 and V, where U_0 is the repulsive energy for two electrons residing at the same site,and V is the corresponding term for inter-site interactions. Then,

$$U = U_0 - V \tag{1.2}$$

is the effective on site Coulomb energy for an electron moving along the chain. In real crystals U also accounts for changes in polarization of the crystal surroundings due to the electron transfer. In the limit of $U \to \infty$, double occupancy of the sites is forbidden. The lower energy band with one state per molecule is then completely filled, and this causes the system to be semiconducting with an energy gap[10]

$$E_g = 2\sqrt{(t_1 - t_2)^2 + \Delta^2} \tag{1.3}$$

The charge alternation $\Delta\rho$ is still given by (1.1), but with p = 2.

So far, we have only considered the $U \to 0$ and $U \to \infty$ limits of a dimeric chain, in which two inequivalent transfer integrals alternate. The chain is defined to be monomeric for the limit of $t_1 \to t_2$. In this case the band gap vanishes for $\Delta \to 0$, which leaves a single band. This band is quarter filled for $U = 0$ and half filled for $U = \infty$, and therefore metallic, irrespective of the value of U.

Simple analytically solvable models are only available for monomeric and dimeric chains satisfying the conditions mentioned above. In the $XY(T)M(TCNQ)_2$ salts, tetrameric stacks are also observed, for which, even for $U = 0$ and $U = \infty$, the band structure must be calculated numerically for known values of the transfer integrals and the potentials at the sites. A model in which this can be done, and that can also cope with intermediate values of U for all types of stacks, utilizes the Hubbart Hamiltonian[12]:

$$H = \sum_{i,\sigma} t_{i,i+1}(c^{+}_{i,\sigma}c_{i+1,\sigma} + c^{+}_{i+1,\sigma}c_{i,\sigma}) + \sum_{i} U\, n_{i,\sigma}n_{i,-\sigma} \qquad (1.4)$$

where c^{+} and c are creation and annihilation operators, and $n_{i,\sigma}(n_{i,-\sigma})$ is a number operator counting the electrons with spin $\sigma(-\sigma)$ at site i. Other parameters can be included in this model as well. Calculations on a finite ring system representing the infinitely long chain, have shown[13], that the properties of the system critically depend upon the ratio of U/t. In the physically qualitative approach of this thesis, though, we will mainly refer to the limiting cases $U = 0$ and $U = \infty$

1.3.2 Phase transitions

One of the typical one-dimensional effects is the instability of the electronic system to lattice distortions with wave vectors that are determined by the band filling. For TCNQ salts, the frequently observed phase transitions are usually attributed to these instabilities.

It was Peierls[14], who first realized that for $U = 0$, a coupling of the electronic structure in a uniform chain to phonons with wave vector $2k_F$ ($k_F = \frac{\pi\rho}{2a}$ is the wave vector of electrons at the Fermi level for a regular chain with periodicity a), causes an energy gap at the Fermi level, which lowers the electronic energy, and thereby stabilizes the distortion. Later it was recognized, that for large U both a $2k_F$[15] and a $4k_F$[16] transition are expected. The observation

of $4k_F$ instabilities in TCNQ salts[17] points to large electron correlations. A qualitative insight in these phase transitions was given by Huizinga[13]. For our purposes it suffices to mention that, by modulating the transfer integral of a monomeric chain, electrons localize and lose part of their entropy at the $4k_F$ or electronic Peierls transition. The transition is therefore observed as a change from metallic to semiconducting or insulating behaviour. At lower temperatures the exchange interaction between the spins is also modofied and spin degrees of freedom are lost at the $2k_F$ or spin Peierls transition. This is reflected in the spin susceptibility, since the ground state of the system changes from magnetic to non-magnetic. It was shown by Landau[18], that in a purely one-dimensional system, long-range order is not possible, and phase transitions are not expected at a finite temperature. However, even a relatively small coupling between the distortions in adjacent chains, which will certainly exist in real crystals, induces a correlation between the chains and long-range order. This effect will produce phase transitions corresponding to the $2k_F$ and $4k_F$ distortions at finite temperatures.

For quarter filled band systems ($\rho = \frac{1}{2}$), such as the XY(T)M(TCNQ)$_2$ salts, the $4k_F$ transition corresponds with a change in stack character from monomeric to dimeric. The stacks in a $2k_F$ distorted phase are expected to be tetramerized. Both phase transitions have been observed in e.g. MEM(TCNQ)$_2$[19], and crystal structure determinations have confirmed the anticipated stack structures for all three phases[20].

1.3.3 Electrical behaviour

Generally, organic substances are poor conductors. The electrical conductivities of the TCNQ salts, however, can, when measured along the stack direction, even reach metallic values[21]. In other directions, conduction is usually several orders of magnitude smaller. In the following, only conduction along the TCNQ stacks is considered.

The electrical conductivity σ is given by

$$\sigma = n e \mu \qquad (1.5)$$

where e is the charge of an electron, and n is the concentration of charge carriers with mobility μ . Most of the XY(T)M(TCNQ)$_2$ salts are semiconducting[22].
The intrinsic conductivity of a pure semiconductor has an exponential dependence on

temperature, because the carrier concentration n is given by

$$n(T) = n_0 \exp(-E_a/kT) \tag{1.6}$$

where the activation energy E_a is half the band gap between the highest filled and the lowest vacant energy level. As to the mobility μ, the situation is more complicated, since there is no general agreement on the transport mechanism in pseudo one-dimensional solids. For band type conduction, μ increases with increasing band width, and it is determined by the scattering of electrons both by thermal vibrations of the lattice and by defects, such as impurities or domain walls. This latter effect is especially drastic in low-dimensional conductors, since in these systems the electrons cannot easily bypass the crystal imperfections.

A consideration of the semiconducting behaviour of the $XY(T)M(TCNQ)_2$ salts in terms of the band model of section 1.3.1 , reveals that the U = 0 case does not apply. In the strongly correlated limit, the band gap is at the Fermi level, yielding an activation energy $E_a = E_g/2$. In this case, high conductivities occur when a small E_a is combined with a large μ, which requires a regular stack with large transfer integrals, and a small variation of the electrical potential at the sites. On the other hand, small conductivities are expected for stacks with a pronounced dimeric or tetrameric character and for stacks with a strongly varying potential.

1.3.4 Magnetic behaviour

The experimental magnetic susceptibility curves $\chi(T)$ of the $XY(T)M(TCNQ)_2$ salts can generally be fitted satisfactorily to theoretical curves, calculated with models that include large values for U. The stacks are represented by one-dimensional Heisenberg spin systems with an antiferromagnetic exchange interactions J between the spins. The models assume complete localization of the spins, and are therefore applicable to complexes in which the stacks are built up from dimers. The electrons are localized at the dimers, and exchange occurs between the dimers.

Bonner and Fisher[23] have calculated the spin susceptibility of such spin systems with a uniform J, which applies to dimerized stacks. J is defined by

$$H = 2J \sum_i \underset{\sim}{S}_i \cdot \underset{\sim}{S}_{i+1} \tag{1.7}$$

where $\underset{\sim}{S}_i$ is the spin operator for $S_i = \frac{1}{2}$, and

$$J = t_2^2/U \tag{1.8}$$

Bulaevskii[24] has given the susceptibility for alternating exchange interactions, which applies to tetramerized ($2k_F$ distorted) stacks. In this case two electrons with opposite spins share the lowest energy level of a tetramer, and at T = 0, there are no unpaired electrons contributing to the susceptibility. The exchange energy is defined by

$$H = 2J \sum_i (\underset{\sim}{S}_{2i} \cdot \underset{\sim}{S}_{2i-1} + \gamma \underset{\sim}{S}_{2i} \cdot \underset{\sim}{S}_{2i+1}) \tag{1.9}$$

where γ is the alternation parameter, and $0 \leqq \gamma \leqq 1$. J is the intra-tetramer and γJ the inter-tetramer exchange interaction. J is given by

$$J = t_1^2/U \tag{1.10}$$

t_1 being the intra-tetramer transfer integral.

Neither of the two models takes into account a non-uniform charge distribution of the unpaired electrons in the TCNQ stacks, but if the non-uniformity is limited to within the dimer, this will only affect the expressions (1.8) and (1.10) when the spin and charge density fluctuations are coupled.

1.4 Summary

To gain insight into the variety of the TCNQ complexes with morpholinium type cations, some 50 new members of this class have been prepared. In section 2.1 the nomenclature of the salts is explained and a survey is given of all complexes known at present. On the basis of an explorative study of crystal chemical properties and physical behaviour, ten of the newly synthesized salts have been selected for a complete X-ray diffraction study. These complexes have a stoichiometry of donor to acceptor of 1:2 and contain the cations HBTM, MBTM, METM, DMM, MPM, MBM, DMTM, HMM, EBTM and EBM. Their crystal structure determinations are described in sections 2.3 - 4. In 5 cases the accuracy of the structures is unfavourably influenced by disorder of the cations.

In chapter 3 the structural details of the XY(T)M$(TCNQ)_2$ salts are

presented. The characteristic stack-sheet structure is demonstrated with the aid of a hypothetical compound $PQM(TCNQ)_2$, which exhibits idealized packing features. On the basis of this structure, descriptive structural parameters are defined for the geometries of the TCNQ stacks, from which the physically relevant transfer integrals t and the charges ρ can be deduced. The descriptive parameters are used to give a compact presentation in figures and tables, of the newly determined structures (section 3.2). Comparison of the structures shows that in a number of cases small changes of the cations have a pronounced influence on the crystal packing and the nature of the stacks.

In chapter 4 all crystal structures known at present for $XY(T)M(TCNQ)_2$ complexes are considered. Attempts have been made to find relations between the structures and electrical conductivities (section 4.2), magnetic susceptibilities (section 4.3) and the occurrence of phase transitions (section 4.4). Classification of the complexes according to their structural characteristics confirmed the physical significance of the t values and the charge distribution along the stacks, and revealed the importance of the overlap type for successive TCNQ molecules. Additionally, it was found that physical properties can be seriously affected by the presence of inequivalent sheets and by the disorder of the cations. In particular, some remarkable physical phenomena have been tentatively attributed to the occurrence of charge transfer between inequivalent sheets, a possibility which has been overlooked so far in the literature on low-dimensional materials. The disorder of the cations may have an especially drastic effect on the phase transitions of the compounds, which demonstrates that the crystal structure as a whole governs the physical behaviour of the complexes. What must be emphasized is, that the classification of the complexes has only given a qualitative insight into the relations between crystal structures and physical properties. This is partly due to the fact that the X-ray data used, only contain information on the average crystal structures, whereas a more profound theoretical knowledge is also required for a more quantitative understanding.

The recognition of the physically relevant factors presented above for known crystal structures does not imply that methods are now at hand to tune the physical properties of the crystals by chemical manipulations. On the contrary, the large variety in structures found for the $XY(T)M(TCNQ)_2$ salts indicates that the prospects for such modifications are poor for this class of compounds.

In chapter 5 a brief introduction is given to diffuse X-ray scattering. By means of this technique, (correlations between) deviations from

average crystal structures can be detected, which is essential for a complete characterization of solid materials. A preliminary set-up for the experiments is described. Some exposures of XY(T)M(TCNQ)$_2$ complexes illustrate the present possibilities of photographic registration of diffuse X-ray scattering in our department.

Chapters 6 and 7 contain crystal structure determinations at low temperatures. The two low temperature modifications of DMM(TCNQ)$_2$ described in chapter 6, reveal that these complexes show unexpected structural changes upon cooling. For the monoclinic form, this is the octamerization of the TCNQ stacks below $T_c \simeq 260$ K, whereas between 200 and 150 K the triclinic modification develops an incommensurable modulation of the DMM molecules. In chapter 7, however, earlier predictions are confirmed. A neutron diffraction study of MEM(TCNQ)$_2$ at 6 K, demonstrates the expected tetramerization of the TCNQ stacks at the spin Peierls transition at 17.4 K. The distortion of the stacks is described by small lateral displacements ($\simeq 0.20$ Å) of the TCNQ dimers relative to each other.

References

1. Recent introductions may be found in
   a. P.Day, Chem.in Brit. 19, 306 (1983).
   b. M.R.Bryce & L.C.Murphy, Nature 309, 119 (1984).
2. Surveys of the chemistry and physics of low-dimensional solids may be found in the following books:
   a. H.J.Keller (ed.), Low Dimensional Cooperative Phenomena (Plenum, New York, 1975).
   b. J.S.Miller & A.J.Epstein (eds.), Synthesis and Properties of Low Dimensional Materials, Ann.N.Y.Acad.Sci. 313, (1978).
   c. L.Alcacer (ed.), The Physics and Chemistry of Low Dimensional Solids (Reidel, Dordrecht, 1980).
   d. Proc.Int.Conf. Physics and Chemistry of Low Dimensional Synthetic Metals (Abano Terme, 1984) Mol.Cryst.Liq.Cryst.(in Press).
3. K.Bechgaard, K.Carneiro, M.Olsen, B.Rasmussen & C.S.Jacobsen, Phys.Rev.Lett. 46, 852 (1981).
4. W.A.Little, Phys.Rev. A134, 1416 (1964).
5. L.R.Melby, A.J.Harder, W.R.Hertler, W.Mahler, R.Benson & W.E.Mochel, J.Am.Chem.Soc. 84, 3370 (1982).